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Major and Trace Elements in Moldavian Orchard Soil and Fruits: Assessment of Anthropogenic Contamination

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Abstract: The correct assessment of the presence of potentially contaminating elements in soil, as well as in fruits cultivated and harvested from the same places has major importance for both the environment and human health. To address this task, in the case of the Republic of Moldova where the fruit production has a significant contribution to the gross domestic product, the mass fractions of 37 elements (Na, Mg, Al, Ca, Si, K, Mn, Fe, Sc, Ti, V, Cr, Co, Ni, Zn, As, Br, Rb, Sr, Zr, Mo, Cd, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Hf, Ta, W, Th, and U) were determined by instrumental neutron activation analysis in soil collected from four Moldavian orchards. In the case of three types of fruits, grapes, apples, and plums, all of them collected from the same places, only 22 elements (Na, Mg, Cl, K, Ca, Sc, Mn, Fe, Co, Ni, Cu, Zn, As, Br, Rb, Sr, Sb, Cs, Ba, La, Th, and U) were detected. The enrichment factor, contamination factor, geo-accumulation index, as well as pollution load index were calculated to assess the soil contamination. At the same time, the metal uptake from the soil into fruits was estimated by means of transfer factors. Soil samples showed for almost all elements mass fractions closer to the upper continental crust with the exception of a slightly increased content of As, Br, and Sb, but without overpassing the officially defined alarm thresholds. In the case of fruits, the hazard quotients for all elements with the exception of Sb in fruits collected in two orchards were below unity. A subsequent discriminant analysis allowed grouping all fruits according to their type and provenance.

Keywords: fruit orchard; metal uptake by plants; potentially hazardous elements; environmental pollution

1. Introduction

The relationship between food and health becomes critically important as consumers now demand healthy, tasty, and natural products, grown in uncontaminated environments [1]. Consequently, the analysis of trace elements in fruits has gained considerable importance, as fruits, rich in

carbohydrates, organic acids, as well as vitamins and minerals, are important components of human diet [2–4]. The potential beneficial health effects of fruits are also attributed to the phenolic compounds related to antioxidant activity [5]. According to [6], the consumption of fruits and vegetables is helpful to reduce the risk of cardiovascular diseases and even prevent cancer. For vegetarians and vegans, the intake of minerals and trace elements from fruits becomes particularly vital [7].

Typical factors affecting the mineral composition of fruits are soil composition, climate conditions (temperature and light intensity), and agricultural practices [8]. Contamination of fruits with potentially hazardous elements may occur due to extensive use of fertilizers and metal-based pesticides. Absorption from the airborne deposits on the aerial parts, as well as from soils through root systems are the main pathway for contaminants. The use of contaminated water in irrigation also represents an important source of excessive accumulation of potentially toxic elements in fruits [3,9].

Assessment of the fruits' chemical composition is important from several points of view: (i) to ensure that the levels of potentially hazardous elements in fruits meet national and international standards; (ii) to permit their differentiation based on their regional origin [3,10,11]. Despite the significant nutritional importance of fruits, the number of studies devoted to their elemental composition, and especially concerning the presence of potentially toxic elements, is relatively few. In this regard, [12] presented the mass fractions of 12 essential and potentially hazardous elements in 98 commercially available fresh fruits in Poland. In [13], the presence of 13 elements including the potential contaminants Co, Cr, Mn, Ni, Cu, Zn, and Pb in three varieties of sour cherry and table grape cultivars was evidenced. As in previous cases, atomic absorption spectrometry was used to assess the levels of Cu, Zn, Cd, and Pb in various fruits sold in Egyptian markets [9].

Among the highest sensitivity and highest accuracy analytical methods, Instrumental Neutron Activation Analysis (INAA) has been successfully used due to its capability to determine the presence of up to 45 different elements simultaneously in a wide range of matrices, including fruits [7,14]. This is done without any previous preparation of the samples, such as acid digestion, which is likely to induce unwanted systematic errors [15,16].

According to the Köppen-Geiger classification [17], the moderately continental climate of the Republic of Moldova can be classified as Dfb with annual rainfall decreasing from 600 mm in the north to about 400 mm in the south. This characteristic, together with an almost ubiquitous presence of high quality chenozem soils, represents favorable conditions for an intensive agriculture and horticulture. For this reason, the Republic of Moldova has gained a good reputation as a supplier of high-quality wines, fruits, and vegetable products in southeastern Europe [18]. This performance is due in great measure to the chernozem, a remarkable type of soil due to its fertility and resilience, which covers almost all the Moldavian territory [19–21]. Here, due to centuries of cropping, a significant part of the humus, the most precious component of chernozem, was lost, which at present requires different organic and inorganic amendments to maintain its fertility.

About two thirds of the agricultural land in Moldova is cultivated by large farms holding more than 100 ha of land and specialized in cereal and technical crops, mainly oriented towards export markets. According to the National Bureau of Statistics of the Republic of Moldova, in the period from 2014–2019, the production of fruits increased from 497 to 840 $\times$ 10^3 tones and of grapes from 594 to 657 $\times$ 10^3 tones [22].

These achievements were possible due to an intensive use of fertilizers and pesticides, sometimes from uncertified sources, which could affect the quality of the soil, as well as of the crops, with negative consequences on human health. For this reason, the main aims of the present research are: (i) to determine, by INAA, the elemental composition of soils and fruits collected in four orchards in the Republic of Moldova and to assess the potential anthropogenic contamination, (ii) to determine the values of the transfer factor and hazard quotients for the investigated fruits, and (iii) to establish to what extent the elemental composition can be useful as a fingerprint to differentiate fruits by region and by type. The results thus achieved, as well as their analysis and discussion are the object of the present study.